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A Phenomenological Approach to Obtaining Correlations between Accelerated and Outdoor Exposure Test Results for Organic Materials

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Abstract: Two approaches are commonly used to derive correlations between in-service and accelerated exposure test results. When detailed degradation mechanisms are well understood, a deterministic formalism can be applied in which a precise damage function model is utilized. If failure mechanisms are not known or multiple mechanisms interact in a complicated manner that makes it difficult and tedious to treat them explicitly, a probabilistic procedure can be used. Observed failures are fit to appropriate life distributions to obtain expressions for related failure rates. A third approach uses a phenomenological methodology. This procedure is similar to the deterministic approach in that damage functions are hypothesized, except that they are based on macroscopic observations and effects, rather than on microscopic mechanisms. The phenomenological approach is used herein to accurately describe results from a number of highly accelerated exposure tests of organic materials. The ensuing damage function models are then used to predict real-world behavior. Excellent agreement is demonstrated between these predictions and actual measured data, thereby validating the phenomenological approach and providing a very useful way to estimate service life of organic-based materials.

Keywords: Accelerated testing, outdoor testing, organic materials, performance degradation, service life prediction

Introduction

Organic materials play an increasingly important role in new and improved product development. Such materials as paints and other organic coatings, adhesives, sealants, bulk polymer parts (including sheets, films, and molded/extruded pieces), fabrics, and foams are used for decorative as well as structural applications within the transportation, construction, biomedical, aerospace, and energy industries. Advantages associated with

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the use of these materials include reduced weight and cost, as well as ease of fabrication, assembly, and installation. A major concern is uncertainties about their durability and related service life prediction (SLP). The technologies for developing and manufacturing products containing organic-based materials are evolving and expanding so rapidly, and competition is so intense, that companies cannot afford to wait for traditional real-time in-service test results. Application of accelerated stress levels can provide greatly abbreviated testing timeframes, but derivation of realistic and believable correlations between accelerated exposure test (AET) results and in-use performance are difficult. Depending on the detailed failure mechanisms associated with particular materials or devices, SLP has usually been based on mechanistic and/or probabilistic principles. The key elements of both of these approaches are reviewed below. Thereafter, a phenomenological methodology is discussed, and examples of its usefulness are presented.

Mechanistic Models

The ability to relate kinetic models of degradation to mathematical formulations of performance-loss distributions enhances product developers' understanding and confidence in SLP. Organic materials are known to be susceptible to degradation caused by cumulative light dosage (D) exposure [1]:

$$D(t) \sim \int_0^t I_{\Delta\lambda}(t') dt' \quad (1)$$

where $I_{\Delta\lambda}(t)$ is the time-dependent irradiance within a specified bandwidth ($\Delta\lambda = \lambda_{\max} - \lambda_{\min}$). $I_{\Delta\lambda}(t)$ can be calculated from the incident spectral irradiance, $I(\lambda, t)$, convolved with the absorption spectra of the material being exposed, $\alpha(\lambda, t)$, and the quantum efficiency of the absorbed photons to propagate reactions that are harmful to the material, $\eta(\lambda, t)$, integrated over an appropriate bandwidth within which light-induced damage occurs:

$$I_{\Delta\lambda}(t) = \int_{\lambda_{\min}}^{\lambda_{\max}} I(\lambda, t) \alpha(\lambda, t) \eta(\lambda, t) d\lambda \quad (2)$$

In general, the activation spectra will be material specific, and considerable effort will be required to obtain $I_{\Delta\lambda}(t)$ [2]. Other environmental stresses such as heat and moisture may also contribute to degradation reactions. Through significant investment of time and resources, it may be possible to identify and model the most important mechanisms that affect a particular material. When changes to the material construction or composition are made, additional effort is required to adequately understand and treat the new material system. Even when it may be possible in principle to identify all degradation mechanisms and to isolate their individual effects along with synergistic

interactions with other stress-induced reactions, it is usually too costly and time consuming, and therefore impractical, to do so.

Probabilistic Models

When failure mechanisms are not known or multiple mechanisms interact in a complicated manner, it may be difficult and tedious to proceed with a deterministic approach. A probabilistic formalism can be used whereby observed failures are fit to life distributions that are characterized by their respective probability density functions (PDF), $f(t)$. This results in an analytical expression for the failure rate, $h(t)$. Life distributions that have proven to be useful in this regard include the exponential, Weibull, and lognormal functions [3]. The failure rate can be obtained from the PDF by first computing the cumulative distribution function (CDF):

$$F(t) = \int_0^t f(t') dt' \quad (3)$$

The failure rate is then:

$$h(t) = \frac{f(t)}{1 - F(t)} \quad (4)$$

A plot of failure rate versus time often resembles the well-known “bathtub” curve. Early in a product’s life, failures can be quite frequent as deficient parts are weeded out. As the sub-population having inadequate initial reliability fail (“infant mortality”), the failure rate rapidly decreases and a long period of stability is reached in which failures occur randomly or at a fairly constant and predictable rate. After an extended period of service, parts begin to wear out and the failure rate rapidly increases, marking the end of the useful life of the product. Materials and components can often be modeled as a series system [4] in which the device has a potential time-to-failure for each of M competing failure modes. The lifetime of such a system is the smallest of those M potential times-to-failure, and the system fails when the first failure mode occurs. If the different times-to-failure associated with the M modes are statistically independent, then the composite failure rate function will follow the addition model for failure rates:

$$h(t) = \sum_{i=1}^M h_i(t) \quad (5)$$

Once the overall failure rate is known, the time, t , at which a specified fraction of units, $F(t)$, still survive can be calculated as [5]:

$$\ln[1 - F(t)] = - \int_0^t h(t') dt' \quad (6)$$

Having a parametric model allows projections to times much earlier than the time of the first observed failure. This is particularly important when 100% / N samples being tested >> some small percentile of the population for which a failure time is desired. Justification of such a probabilistic approach should be based primarily on the fact that it works, that is, that the chosen distribution fits the data well and that it leads to reasonable projections when extrapolating beyond the range of the data. Ideally, the selection and use of a particular life distribution should be further justified by theoretical considerations. For example, a lognormal distribution can be shown to be theoretically applicable to chemically induced failure mechanisms such as corrosion, diffusion, or electromigration [3]. As such, the lognormal distribution typically provides a good representation of the wearout segment of the failure rate curve. While the probabilistic approach can allow useful estimates of service life to be made, it may not provide an understanding of why materials are failing or how improvements can be implemented.

Phenomenological Approach

Another way to obtain correlations between in-use and accelerated exposure results is a non-mechanistic or phenomenological methodology. This procedure is similar to the deterministic approach in that damage functions are hypothesized, except that they are based on macroscopic observations and effects, rather than on microscopic mechanisms. For example, the impact of light exposure may be known to cause degradation of a certain material, and so a model is developed that accounts for this stress factor without necessarily expressing an understanding of the detailed reactions that may proceed at a microscopic level [6]. The general sequence of this approach includes the following steps:

- 1) Perform accelerated screening tests to determine: a) important/relevant stresses and b) an appropriate response variable.
- 2) Carry out appropriate analytical characterizations to ensure that unrealistic failure mechanisms do not occur and to thereby establish upper levels of accelerated stresses.
- 3) Based upon accelerated screening tests, hypothesize a model that relates applied stresses to changes in performance (form of damage function).
- 4) Perform well-designed factorial experiment to obtain values for the damage function coefficients.
- 5) Use monitored real-world stresses and measured response variable data to validate the model.
- 6) Use validated model and long-term (or stochastically generated [7]) data sets to predict lifetime at in-use environmental conditions of interest.

It is important to obtain a suitable material-specific damage function model that accurately relates changes in an appropriate response variable to relevant applied environmental stresses. Exposure tests of organic materials as polymer sheet [6] and back-metallized polymer film [8,9] have provided useful results by approximating the absorption spectra and quantum efficiency as an aggregated constant, B, in Equation 2 and defining:

$$I_{\Delta\lambda}(t) = B \int_{\lambda_{\min}}^{\lambda_{\max}} I(\lambda, t) d\lambda \quad (7)$$

with $\lambda_{\min} = 285$ nm and $\lambda_{\max} = 315$ nm (for $\Delta\lambda = \text{UV-B}$) or $\lambda_{\min} = 290$ nm and $\lambda_{\max} = 385$ nm (for $\Delta\lambda = \text{total UV}$). These spectral ranges are chosen to facilitate comparison with monitored outdoor light exposure test data because they correspond to typical response bandwidths of commercial UB-V and total UV pyranometers. For constant (controlled) irradiance, this leads to an approximate generalized cumulative dosage model in which the loss in performance, ΔP (change in response variable), with time is proportional to a power-law expression of the ultraviolet irradiance, I_{UV} [9,10]:

$$\frac{\Delta P}{\Delta t} \sim (I_{\text{UV}})^n \quad (8)$$

To account for thermal effects, an Arrhenius term can be included [3], and the change in performance after the i^{th} time interval is:

$$\Delta P_i = A (I_{\text{UV}})^n \Delta t_i e^{-E/kT} \quad (9)$$

where T is the temperature (K) experienced by samples during exposure, k is Boltzmann's constant, and E is an activation energy. For constant accelerated stresses, I_{UV} and T are known; this allows Equation 9 to be fit to measured values of ΔP_i and subsequent determination of the coefficients A, E, and n. For variable real-world stresses, the time-dependent form of Equation 9 must be used:

$$\Delta P(t) = A \int_0^t [I_{\text{UV}}(t')]^n e^{-E/kT(t')} dt' \quad (10)$$

Having determined the relevant coefficients from accelerated exposure tests performed at constant stresses, Equation 10 can be used to compute a predicted loss in performance after some time t, where the relevant stresses are monitored during in-use conditions; these predicted values can then be compared with actual measured values. This approach has been implemented to demonstrate its usefulness and validity for organic glazing and reflector materials.

Application of Phenomenological Approach to Organic Materials

Polymeric Glazings

Values of ΔP_i were measured for samples of glazing materials exposed outdoors while the relevant time-dependent stress variables were monitored. Thus, Equation 10 could be used to predict ΔP_i for comparison with measured data. To validate the methodology presented above, two types of sheet (0.32 cm-thick) glazing materials tested at two outdoor exposure test (OET) sites were considered. These include polyvinyl chloride (PVC) and a UV-stabilized polycarbonate (PC). These materials were also exposed in accordance with the ASTM Practice for Operating Xenon-Arc Type Light Exposure Apparatus With and Without Water for Exposure of Plastics (D 2565) within an accelerated exposure chamber (having a UV intensity of about 2X compared to typical outdoor terrestrial levels), and at 50X and 100X using a UV concentrator [6]. The response variable was chosen to be hemispherical transmittance between 400 and 500 nm because, in general, that is the spectral region most sensitive to stress exposure-induced loss in performance. The damage functions expressed in Equations 9 and 10 were assumed. Data from the accelerated weathering chamber and the UV concentrator exposures were used to fit Equation 9 and to obtain the model coefficients; the results are given in Table 1. Values of activation energies (E) derived are reasonable for photo-thermally driven degradation mechanisms. A value of $n \sim 2/3$ for PVC implies that exposure to 50-100X light intensities had a net effect of only 15-25X, suggesting that some shielding or rate-limiting reactions occur that do not allow all photons to participate in degradation. For the UV-stabilized PC sample, a value of $n=1$ suggests that exposure of this material follows strict reciprocity even up to 100X; all incident photons fully contribute to degradation reactions that proceed at twice the rate experienced at 50X exposure and 50 times the rate experienced at 2X exposure.

Table 1. Damage function coefficient values derived for representative clear polymer sheet samples.

<i>Polymer Sheet</i>	<i>A</i>	<i>n</i>	<i>E (kcal/mole-K)</i>
Polyvinyl Chloride	2892	0.669	8.440
UV-Stabilized Polycarbonate	5.497	1.093	6.688

Using the coefficients from Table 1 and time-monitored values of sample temperature and UV irradiance, the loss in performance was predicted using Equation 10 for both PVC and PC as exposed outdoors in Golden, CO, and Phoenix, AZ. Predicted values were then compared with actual measured data for these materials exposed at these sites. The results are presented below (Figure 1). Time-dependent changes in weathering variables produce the irregular shapes of the predicted curves. Excellent agreement is evident between the measured and predicted data, thereby validating both

the phenomenological approach to data analysis (using accelerated test results to obtain model coefficients, and then the use of these coefficients to predict time-variable real-world degradation), and the assumed damage function model.

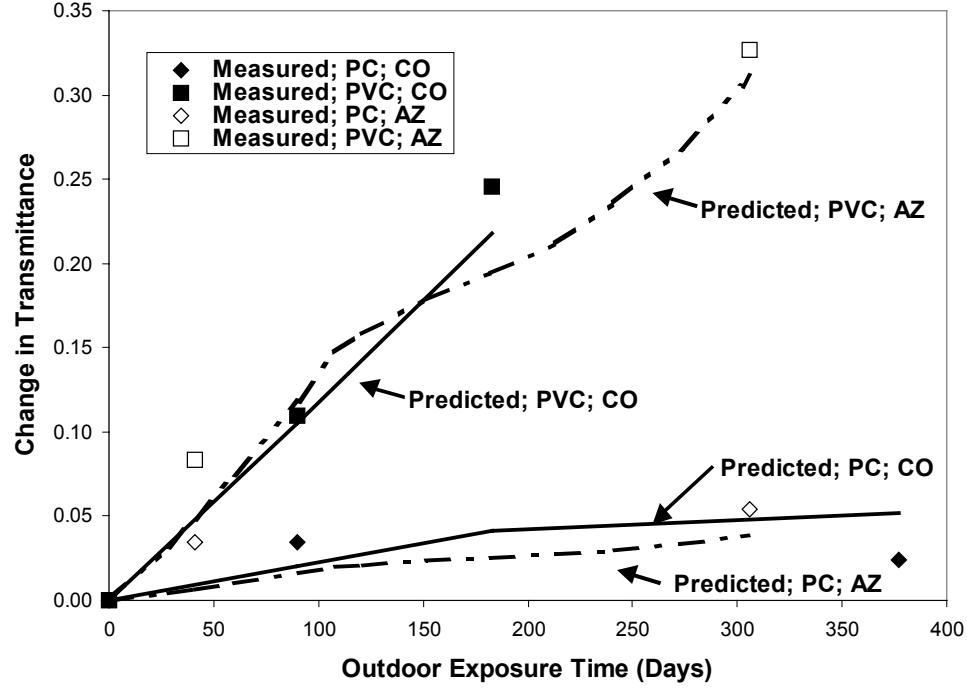


Figure 1. Measured vs. predicted change in hemispherical transmittance between 400 and 500 nm for two polymeric materials exposed at two outdoor test sites.

Metallized Polymers

The approach outlined above was slightly modified to allow moisture effects to be included in the analysis of metallized polymer reflector materials. A model developed in [9] that relates the time-dependent loss in performance (degradation in hemispherical reflectance at 400 nm), $\Delta\rho_{400}(t)$, to relevant environmental stresses was used:

$$\Delta\rho_{400}(t) = A \int_0^t I_{UV}(t') e^{-E/kT(t')} e^{C \cdot RH(t')} dt' \quad (11)$$

where:

$RH(t)$	=	time-dependent ambient relative humidity (%)
A, E, C	=	material-dependent coefficients to be determined from measured data.

Note that for the metallized polymer data considered, the exponent, n , in Equation 10 was consistently unity in Equation 11 and so was set equal to one. Reflectance at 400 nm was chosen as the performance parameter because it provides a particularly sensitive indicator of degradation [9]. This response variable is a measure of corrosion at the metal/polymer interface. Light is believed to initiate photochemical reactions within the bulk polymer film; reactant species then reach (by diffusion and/or moisture transport) the metal interface, where corrosion and subsequent loss of reflectance occurs. $I_{UV}(t)$ is obtained by integrating the spectral irradiance in the UV-B bandwidth, as given by Equation 7. The UV-B bandwidth is emphasized because light in this spectral range has been found to be most deleterious to metallized polymer reflector materials of interest.

Time-dependent I_{UV} data were recorded and available from an UV-B pyranometer deployed at outdoor test sites. Temperature and relative humidity data were also measured/monitored at these sites. For discrete time intervals, the degradation in performance was computed as the sum of the coincident temporal variations of the appropriate environmental stresses:

$$\Delta p_{400}(t) = A \sum_t I_{UV}(t) e^{-E/kT(t)} e^{C \cdot RH(t)} \Delta t \quad (12)$$

Equation 12 is also applicable for tests of materials exposed to laboratory-controlled conditions. If the various relevant environmental stresses are controlled to be at constant levels, the loss in performance after some cumulative exposure time, Δt , will be:

$$\Delta p_{400}(t) = A I_{UV} e^{-E/kT} e^{C \cdot RH} \Delta t \quad (13)$$

By performing a series of laboratory experiments for which Equation 13 is valid, the coefficients A , C , and E were obtained. The procedure was to apply constant levels of stresses (I_{UV} , T , and RH) to materials of interest and then to measure the loss in performance, $\Delta p_{400}(t)$, at periodic intervals, Δt . Note that $\Delta p_{400}(t)$ must be measured at several levels of each stress in order for the coefficient associated with that stress to be determined. For example, if only one temperature is used, then the effect of the $e^{-E/kT}$ term will be constant and can be accounted for by (combined with) the coefficient A . The best approach is to use a factorial-designed experiment in which at least two levels of each stress of interest (for example, T_{high} and T_{low}) are tested. Sample exposure chambers that allow two levels each of temperature and relative humidity to be concurrently applied to samples during exposure to a common level of light intensity have been designed and used for exposure testing (Figure 2). This allows a four-fold increase in experimental throughput. Furthermore, by using elevated levels of applied stresses (with assurances that the stresses are not accelerated to the extent that unrealistic failure mechanisms are introduced), measurable degradation can be achieved in very abbreviated timeframes, allowing estimates of relevant coefficients to be determined rapidly. Once the coefficients are known, they can be used in Equation 12, along with meteorological data monitored at geographical locations of interest, to compute performance loss as a function of time. By defining failure as the loss in performance below some desired or preferred level, the associated service lifetime can be predicted. Alternatively, if measured data are available

for a given site at which meteorological data are also available, Equation 12 can be used to validate the methodology for predicting material lifetimes.

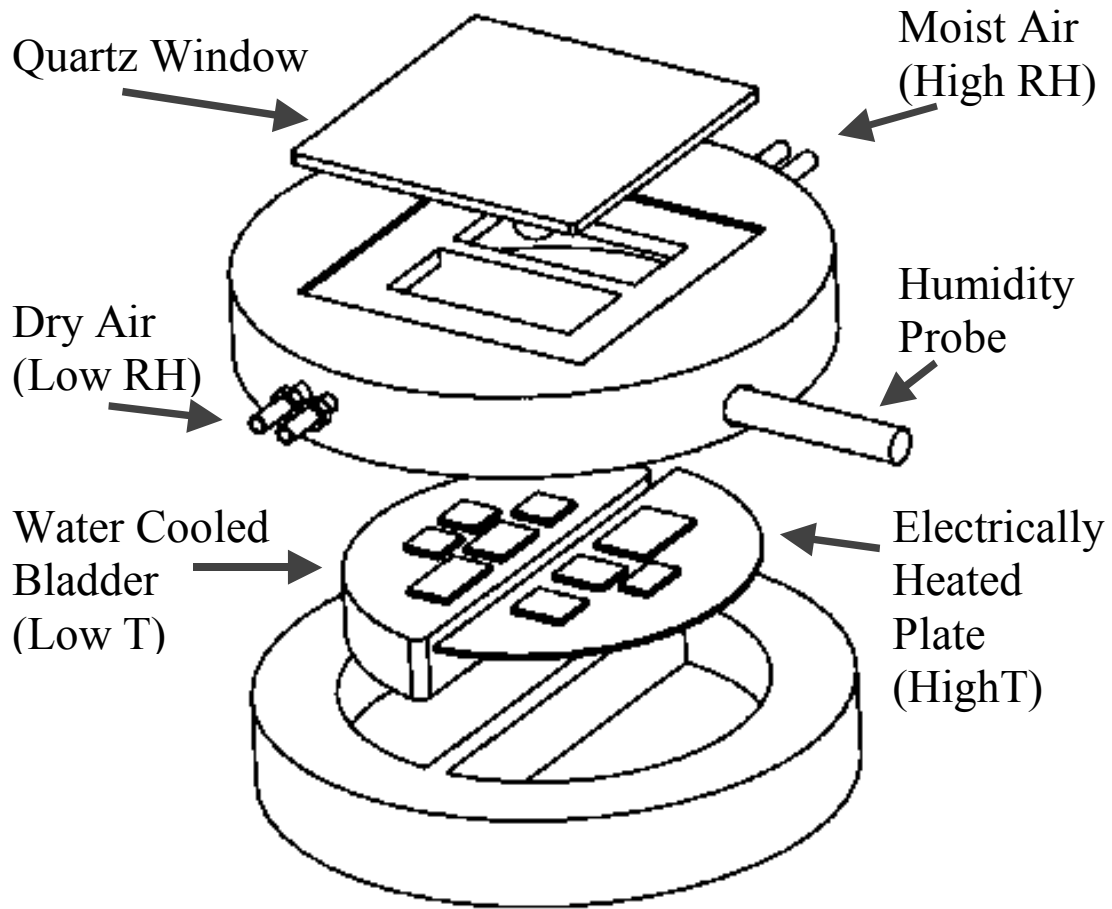


Figure 2. Exposure chamber allowing concurrent multiple levels of light, temperature, and relative humidity.

A material under exposure at OET sites was subjected to ultra-accelerated levels of natural sunlight at NREL's High Flux Solar Furnace (HFSF), with I_{UV} being 50, 75, and 100 suns [8]. This material, a silvered polymer reflector product, has the construction:

Polymer Film Superstrate / Reflective Layer / Adhesive / Substrate

where the polymer film superstrate was an 89 μm -thick polymethylmethacrylate (PMMA) film, the reflective layer was 0.1 μm silver, and the substrate was 6061 sheet aluminum.

Data from these experiments were fit to Equation 13 to obtain the coefficients A, C, and E, as compiled in Table 2.

Table 2. Damage function coefficient values derived for metallized polymer film.

<i>Coefficient</i>	<i>Value</i>
A	2.27×10^{-5}
C	0.0073
E (kcal/mole-K)	2.74

These parameters were then used in Equation 12 to compute the loss in performance based on actual measured, time-varying environmental stresses measured at the sites at which materials were exposed to real-world environmental conditions. An OET meteorological database was used to obtain tables of hourly averages of I_{UV} , T and RH. Results for two locations, NREL (Golden, CO) and the Sacramento Municipal Utility District (SMUD, in Sacramento, CA), are shown below (Figure 3). The square symbols are measured values of hemispherical reflectance at 400 nm for samples exposed at NREL, and the circle symbols are measured values for samples exposed at SMUD. Error bars are \pm one standard deviation. The solid line is the predicted reflectance calculated from Equation 12.

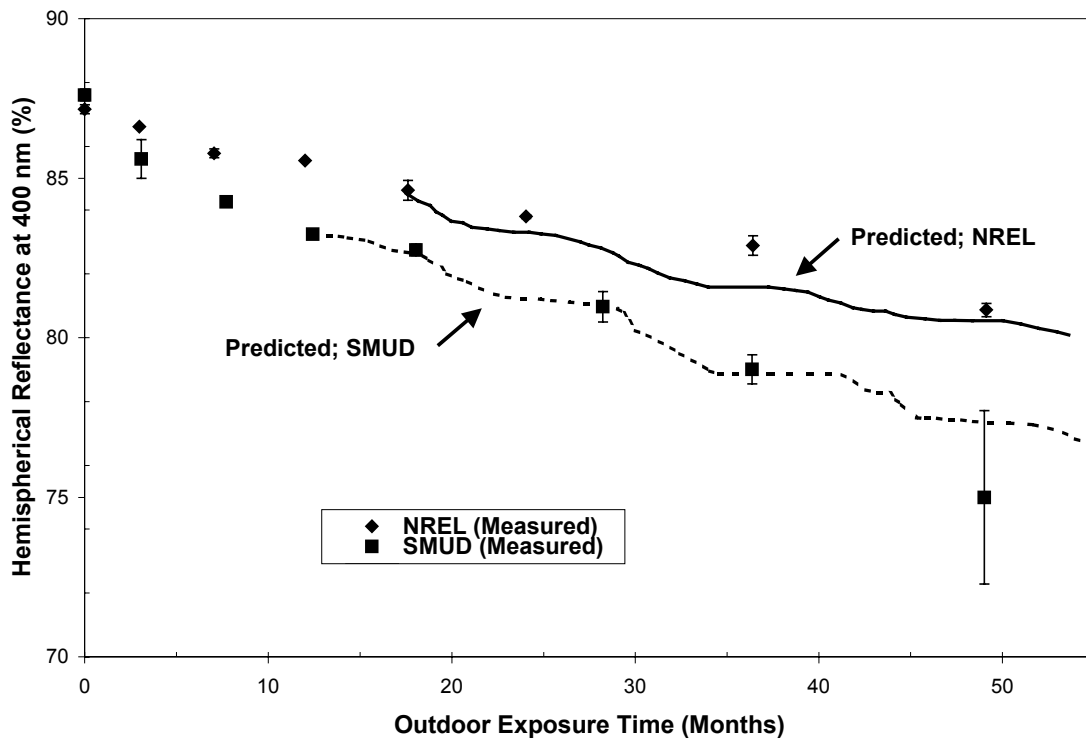


Figure 3. Measured vs. predicted hemispherical reflectance at 400 nm for metallized polymer samples exposed at two outdoor test sites.

As indicated (Figure 3), exposure of samples was initiated before routine acquisition of meteorological data was begun. Therefore, the predicted data were renormalized to the first measurement made after meteorological data were available. Excellent agreement between the predicted and measured data is seen for the metallized

polymer samples exposed at both sites. This demonstrates the usefulness of the phenomenological methodology as applied to metallized polymer reflector materials.

Conclusions

A practical approach to obtain correlations between accelerated and outdoor exposure test results has been demonstrated and validated for several optical elements comprised of representative organic materials. The procedure is based on phenomenological principles, but does not rely on a detailed understanding and analysis of microscopic mechanisms that lead to degradation. However, it does rely on a knowledge of the macroscopic relationship between applied stresses and their effects on relevant response variables. In this regard, this approach may be more palpable than probabilistic treatments and more readily allow product improvements to be made. A straightforward method has been outlined that allows determination of coefficients that relate applied stresses to response variables in the damage function. Once validated, the fully developed damage function can then be used with monitored or statistically generated real-world variable weather data to allow loss in performance to be predicted with confidence.

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